



# Recent progress in photocatalytic conversion of carbon dioxide over gallium oxide and its nanocomposites

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Photocatalytic conversion of CO<sub>2</sub> is a promising method to solve problems of both energy crisis and global climate change. The efficient transfer of solar energy into high-value chemical energy is the ultimate goal of this technology. Gallium oxide is a suitable candidate for the photocatalytic conversion of CO<sub>2</sub> due to its ideal band positions. Modification of Ga<sub>2</sub>O<sub>3</sub> to achieve enhanced photocatalytic activity and understanding the catalytic mechanism are important for the design of high-efficiency photocatalysts.

## Addresses

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## Introduction

The global energy crisis is continually growing due to the use of non-renewable energy sources, such as fossil fuels. Consequently, excessive carbon dioxide (CO<sub>2</sub>) from the consumption of these fossil fuels are released into the atmosphere. This directly exacerbates the greenhouse effect and global warming [1]. It is of great urgency to solve both the energy crisis and global warming and thus mitigate environmental and economic disasters. Therefore, the development of renewable energy technologies is essential for a reliable and sustainable energy supply [2]. Sunlight is the most abundant renewable energy source as it is clean, non-monopolized, and environmentally friendly. Harvesting, storage, and practical utilization of solar energy are critical worldwide issues that must be overcome for the widespread adoption of solar energy [3]. Recently, the capture, storage, and utilization of CO<sub>2</sub>,

directly or indirectly, using solar energy have been attempted to mitigate CO<sub>2</sub> emissions and solve energy crisis simultaneously [4].

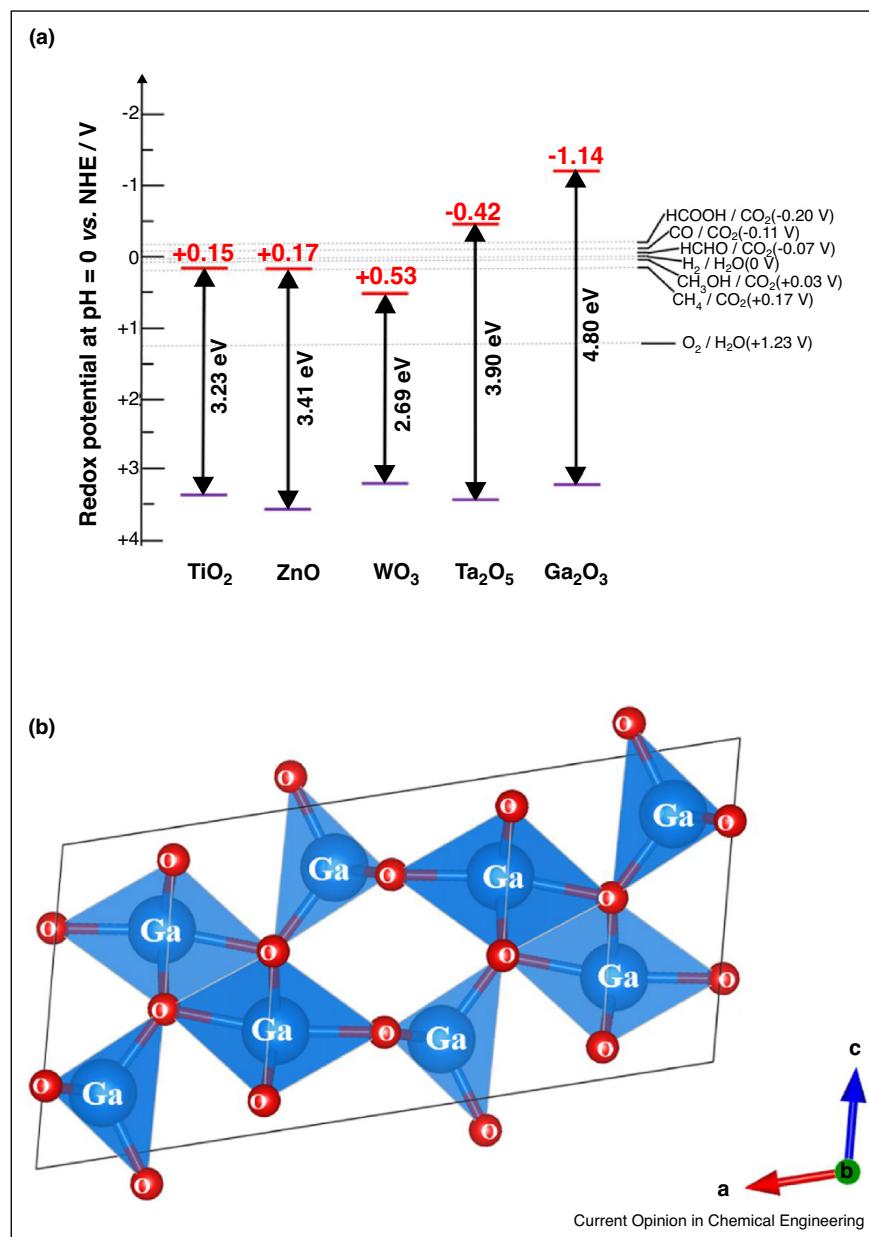
The photocatalytic conversion of CO<sub>2</sub> to chemical feedstocks and hydrocarbon-based fuels is a promising method to simultaneously alleviate the global energy crisis and global warming [5]. Specifically, the photocatalytic conversion of CO<sub>2</sub> using H<sub>2</sub>O as an electron donor by heterogeneous catalysts would be ideal, but achieving efficient catalysis under these conditions has proven to be of great challenges. This reaction is an uphill reaction, taking the conversion of CO<sub>2</sub> using H<sub>2</sub>O to CO, O<sub>2</sub> and H<sub>2</sub> as an example, the standard Gibbs free energy change ( $\Delta G^\circ$ ) of this reaction is +270 kJ mol<sup>-1</sup>. Therefore, solar energy can be converted and stored as chemical energy. Because of the uphill barriers, this reaction is more difficult to achieve as compared to traditional photocatalytic degradation reactions, which normally are downhill reactions ( $\Delta G^\circ < 0$ ) [6]. To date, developments in the photocatalytic conversion of CO<sub>2</sub> are still at a very early stage. Nevertheless, a variety of photocatalysts have been developed that achieve the conversion of CO<sub>2</sub> by H<sub>2</sub>O to carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCHO), methanol (CH<sub>3</sub>OH), and methane (CH<sub>4</sub>) [7].

As a representative photocatalyst, gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) has been recently investigated for the photocatalytic conversion of CO<sub>2</sub>. Generally, Ga<sub>2</sub>O<sub>3</sub> exists as polymorphs  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$  [8,9<sup>•</sup>]. Among these polymorphs,  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has been widely investigated due to its thermodynamically stability [10,11].  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is a semiconductor with a wide band gap of ~4.8 eV. The conduction band (CB) position of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> is much more negative than other selected metal-oxide photocatalysts, such as TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, and Ta<sub>2</sub>O<sub>5</sub> (Figure 1a) [12–15]. This makes  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> to be promising for the photocatalytic conversion of CO<sub>2</sub> because it can provide more negative potential for reduction of CO<sub>2</sub> than others. In this short review, we will discuss the use of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> and its modification for the photocatalytic conversion of CO<sub>2</sub>.

## Brief introduction of Ga<sub>2</sub>O<sub>3</sub> and its preparation methods

Various methods have been used for the fabrication of Ga<sub>2</sub>O<sub>3</sub> nanoparticles, such as sol–gel method [16], chemical vapor deposition (CVD) [17], precipitation method

Figure 1



(a) Conduction (red) and valence (purple) band positions (at pH = 0 versus NHE) of the selected oxide photocatalysts. The values adapted from Ref. [12–15]. (b) is the crystal structure of β-Ga<sub>2</sub>O<sub>3</sub> from Ref. [23].

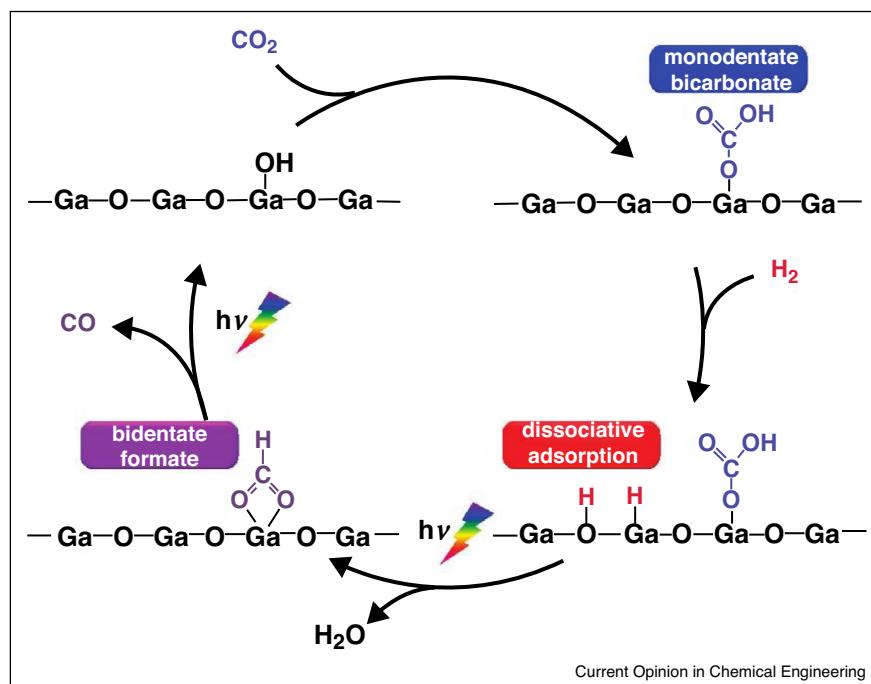
[18], and hydrothermal method [19,20]. Ga<sub>2</sub>O<sub>3</sub> powder used for the photocatalytic conversion of CO<sub>2</sub> is usually fabricated by the calcination of the precursor of co-precipitated gallium nitrate and ammonia solution [21\*,22]. This process allows for the formation of β-Ga<sub>2</sub>O<sub>3</sub>, which contains tetrahedral and octahedral Ga ions (Ga<sup>3+</sup>) in its structure (Figure 1b) [23]. Tetrahedral Ga<sup>3+</sup> is believed to form Lewis acid sites [24], other polymorphs such as α-Ga<sub>2</sub>O<sub>3</sub> with only octahedral Ga<sup>3+</sup> structure cannot form Lewis acid sites [9\*]. Typically, the fabricated Ga<sub>2</sub>O<sub>3</sub>

comprises irregular nanoparticles with elliptical rod-shaped and/or spindle-like morphologies. The Brunauer–Emmett–Teller (BET) specific surface areas of these Ga<sub>2</sub>O<sub>3</sub> particles have been reported to be ~10–40 m<sup>2</sup> g<sup>-1</sup> [20,25,26\*\*,27\*\*].

### Photocatalytic conversion of CO<sub>2</sub> using CH<sub>4</sub> or H<sub>2</sub> as an electron donor

Ga<sub>2</sub>O<sub>3</sub> has been investigated as an active catalyst for the hydrogenation of CO<sub>2</sub> for more than 20 years [28–30].

Figure 2



Schematic mechanism of photocatalytic conversion of  $\text{CO}_2$  over  $\text{Ga}_2\text{O}_3$  in the presence of  $\text{H}_2$ .  
Reprinted with permission from Ref. [33\*\*]. Copyright (2010) American Chemical Society.

However, the first successful photocatalytic conversion of  $\text{CO}_2$  using a  $\text{Ga}_2\text{O}_3$  catalyst was reported by Yuliati *et al.* [31], who demonstrated the photocatalytic conversion of  $\text{CO}_2$  using  $\text{CH}_4$  as an electron donor with a 300 W Xe lamp irradiation.  $\text{H}_2$  and  $\text{CO}$  were the main products of this reaction. In this system, the input of thermal energy is necessary to achieve  $\text{CO}_2$  dry reforming of methane (DRM). Therefore, this report can be classified as thermal-photocatalytic processes for the conversion of  $\text{CO}_2$ .

In late 2008, Teramura *et al.* [21\*] reported the first example of the  $\text{Ga}_2\text{O}_3$  photocatalytic conversion of  $\text{CO}_2$  using  $\text{H}_2$  as an electron donor with a 200W Hg–Xe lamp irradiation.  $\text{CO}$  was the only detected reduction product of  $\text{CO}_2$ .  $\alpha\text{-Ga}_2\text{O}_3$ ,  $\beta\text{-Ga}_2\text{O}_3$ , and  $\gamma\text{-Ga}_2\text{O}_3$  were all reported to show photocatalytic activity toward the conversion of  $\text{CO}_2$  using  $\text{H}_2$  as an electron donor. Of the various polymorphs,  $\beta\text{-Ga}_2\text{O}_3$  calcined at 1073 K showed the highest catalytic activity in the study. The conversion efficiency of  $\text{CO}_2$  was approximately 3%, and it was found that the adsorption of  $\text{H}_2$  onto the  $\beta\text{-Ga}_2\text{O}_3$  particles enhanced the photocatalytic activity. In 2011, Ahmed *et al.* [32] reported that commercial  $\text{Ga}_2\text{O}_3$ , containing mainly  $\alpha$  phase, showed photocatalytic activity for the formation of  $\text{CO}$ , with  $\text{H}_2$  as an electron donor.

Tsuneoka *et al.* [33\*\*] investigated the adsorbed species of  $\text{CO}_2$  and  $\text{H}_2$  on  $\text{Ga}_2\text{O}_3$  for the photocatalytic conversion of

$\text{CO}_2$  with a 200W Hg–Xe lamp irradiation using Fourier transform infrared spectrometer (FT-IR) (Figure 2). Monodentate bicarbonate species were found to be reduced by the dissociatively adsorbed  $\text{H}_2$  under photo-irradiation on the surface of the  $\text{Ga}_2\text{O}_3$  particles. The decomposition of the generated bidentate formate on  $\text{Ga}_2\text{O}_3$  resulted in the formation of  $\text{CO}$  during photoirradiation. The dissociatively adsorbed  $\text{H}_2$  on the  $\text{Ga}_2\text{O}_3$  particles is key for enhancing the photocatalytic activity for the conversion of  $\text{CO}_2$ .

### Photocatalytic conversion of $\text{CO}_2$ using $\text{H}_2\text{O}$ as an electron donor

When  $\text{H}_2\text{O}$  is used as an electron donor, oxidation of  $\text{H}_2\text{O}$  to yield protons and molecular oxygen is necessary for the photocatalytic conversion of  $\text{CO}_2$ . However, water splitting is preferable in terms of energy production than that of conversion of  $\text{CO}_2$ . Therefore,  $\text{H}_2$  is usually the main reduction product, even in the presence of  $\text{CO}_2$  [34]. When  $\text{CO}_2$  is converted to  $\text{CO}$ , the selectivity toward  $\text{CO}$  evolution can be expressed as follows:

$$\text{Selectivity toward CO (\%)} = 100 \times \frac{2R_{\text{CO}}}{2R_{\text{CO}} + 2R_{\text{H}_2}}$$

where  $R_{\text{CO}}$  and  $R_{\text{H}_2}$  represent the rates of  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{O}_2$  formation, respectively. If other reduction products are

formed, their formation rates multiplied by the number of consumed electrons should be added to the numerator and denominator. Bare Ga<sub>2</sub>O<sub>3</sub> was reported to show photocatalytic activity for the conversion of CO<sub>2</sub> to CO in and by H<sub>2</sub>O with *c.a.* 6–14% selectivity toward CO evolution. The formation rates of CO were also limited to a few  $\mu\text{mol h}^{-1}$  or less [22,35,36]. These results indicate that water splitting to H<sub>2</sub> occurs as the main reaction even in the presence of CO<sub>2</sub>. Thus, the modification of the Ga<sub>2</sub>O<sub>3</sub> particles is necessary to achieve enhanced selectivity and photocatalytic activity for the conversion of CO<sub>2</sub> using H<sub>2</sub>O as an electron donor.

Bulk Ga<sub>2</sub>O<sub>3</sub> shows limited catalytic activity due to the small amount of photocatalytic active sites due to the small BET surface area, which in turn results from high-temperature calcination. Park *et al.* [25] designed highly porous bulk Ga<sub>2</sub>O<sub>3</sub> to overcome this limitation, and the fabricated highly porous Ga<sub>2</sub>O<sub>3</sub> showed high CO<sub>2</sub> affinity. Moreover, it was found that CH<sub>4</sub> was the major product of conversion of CO<sub>2</sub> with H<sub>2</sub>O vapor using a 300 W Xe lamp irradiation. Larger surface areas and adsorption capacity are thought to be the reason for the enhanced photocatalytic activity compared to that of bulk Ga<sub>2</sub>O<sub>3</sub>.

Co-catalysts are important for promoting the separation and migration of photogenerated electrons and holes [37], activation of the adsorbed CO<sub>2</sub> [38], and directing the production of reduction products [39]. The activity and selectivity toward the photocatalytic conversion of CO<sub>2</sub> in H<sub>2</sub>O are enhanced using various types of co-catalysts [40]. Ag is one of the most effective co-catalysts for achieving high activity and selectivity toward CO evolution. Both the activity and selectivity are enhanced when Ag is used as a co-catalyst loaded on Ga<sub>2</sub>O<sub>3</sub> [22,35,36].

Recently, Yamamoto *et al.* [35,41] found that small Ag clusters on Ga<sub>2</sub>O<sub>3</sub> showed increased activity and selectivity toward CO evolution with a 300 W Xe lamp irradiation. They demonstrated that smaller Ag clusters accepted more electrons in their d-orbitals as result of the strong interaction with the Ga<sub>2</sub>O<sub>3</sub> surface. The FT-IR results showed that Ag promoted the transformation of bidentate carbonates to form bidentate formates under photoexcitation. Further investigation indicated that structure of the Ag co-catalyst on the surface of Ga<sub>2</sub>O<sub>3</sub> showed aggregation, and that partial Ag<sup>+</sup> were converted to metallic Ag<sup>0</sup> [36]. These changes resulted in a significant effect on the photocatalytic activity and selectivity toward CO evolution. In addition, the same group reported that the coexistence of the  $\gamma$ -phase and  $\beta$ -phase of Ga<sub>2</sub>O<sub>3</sub> showed higher activity for CO production without Ag co-catalyst as compared that with the Ag co-catalyst [42]. It was proposed that the original crystalline structure is changed with the loading of Ag, which deactivates the photocatalytic activity. It should be noted that this was not the case for pure  $\beta$ -phase Ga<sub>2</sub>O<sub>3</sub> where the loading of Ag resulted

in significantly enhanced photocatalytic activity and selectivity toward CO evolution.

Pan *et al.* [20] reported that Pt-nanoparticle-dispersed Ga<sub>2</sub>O<sub>3</sub> nanoparticles showed good photocatalytic activity for CO<sub>2</sub> conversion in H<sub>2</sub>O in a closed system with a 300 W Xe lamp. The highest formation rates of CO, H<sub>2</sub>, and O<sub>2</sub> achieved were 21.0, 36.2, and 7.9  $\mu\text{mol h}^{-1}$ , respectively, resulting in a selectivity toward CO of 36.7%. The selectivity toward CO showed significant enhancement compared to that of bare Ga<sub>2</sub>O<sub>3</sub>. Tiny amounts of CH<sub>4</sub>, CH<sub>3</sub>OH, HCHO, and HCOOH were also detected as reduction products in addition to CO.

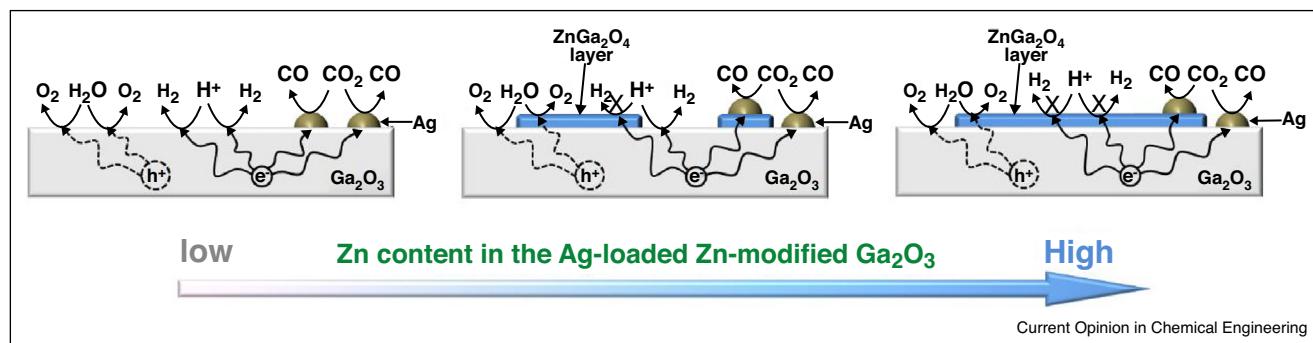
### **Ga<sub>2</sub>O<sub>3</sub> nanocomposites for the enhanced photocatalytic activity**

Even in the presence of a co-catalyst, the activity and/or selectivity toward CO evolution in the photocatalytic conversion of CO<sub>2</sub> by H<sub>2</sub>O over Ga<sub>2</sub>O<sub>3</sub> is limited. Therefore, further modification of Ga<sub>2</sub>O<sub>3</sub> is necessary to achieve higher activity and selectivity. Because Ga<sub>2</sub>O<sub>3</sub> has a wide band gap, the conductivity band (CB) and valance band (VB) positions are not limitations in the reduction of CO<sub>2</sub> and oxidation of O<sub>2</sub> (Figure 1a). The suppression of H<sub>2</sub> generation, increasing the ability of CO<sub>2</sub> adsorption and increasing active sites for the conversion of CO<sub>2</sub> are important for achieving enhanced photocatalytic activity and selectivity.

Wang *et al.* [43] reported the use of Ga<sub>2</sub>O<sub>3</sub> modified with ZnGa<sub>2</sub>O<sub>4</sub> nanoparticles as a heterojunction photocatalyst for the conversion of CO<sub>2</sub> to CH<sub>4</sub> with H<sub>2</sub>O vapor in a closed system with a UV-enhanced (200–350 nm) 300 W Xenon arc lamp irradiation. This heterojunction photocatalyst showed higher photocatalytic activity for the production of CH<sub>4</sub> compared with that of the bare Ga<sub>2</sub>O<sub>3</sub> and ZnGa<sub>2</sub>O<sub>4</sub>. It was concluded by the authors that the formation of the heterojunction improved the separation of photogenerated electron-hole pairs resulting in increased selectivity toward CH<sub>4</sub> evolution.

Teramura *et al.* [22] succeeded in designing a highly selective photocatalytic conversion of CO<sub>2</sub> to CO in and by H<sub>2</sub>O over Ag modified, Zn-doped Ga<sub>2</sub>O<sub>3</sub> in a continuous flow system using a 400 W Hg lamp. The selectivity toward CO was enhanced from 26.4 to 87.4% by doping with 3.0 mol% of Zn in Ga<sub>2</sub>O<sub>3</sub>. Molecular O<sub>2</sub> was stoichiometrically evolved, moreover, isotopic labeling experiments showed that the formed <sup>13</sup>CO originated from the introduced <sup>13</sup>CO<sub>2</sub>. These results clearly showed that H<sub>2</sub>O acts as an electron donor during the photocatalytic conversion of CO<sub>2</sub>, which is important as overall water splitting to produce H<sub>2</sub> are common when using H<sub>2</sub>O as an electron donor [44,45]. Further investigations revealed that the selectivity toward CO over H<sub>2</sub> can be controlled by varying the amount of Zn dopant in the Ga<sub>2</sub>O<sub>3</sub> [26<sup>••</sup>]. It was confirmed that a ZnGa<sub>2</sub>O<sub>4</sub> layer was generated on the surface of the Ga<sub>2</sub>O<sub>3</sub> by the addition of

Figure 3



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Proposed mechanism for the photocatalytic conversion of  $\text{CO}_2$  in and by  $\text{H}_2\text{O}$  over Zn modified  $\text{Ga}_2\text{O}_3$  with changing Zn content. Reproduced from Ref. [26<sup>\*\*</sup>] with permission from The Royal Society of Chemistry.

Zn species. The  $\text{ZnGa}_2\text{O}_4$  layer suppresses the reduction of  $\text{H}^+$ , significantly enhancing the selectivity toward CO with increased Zn content (Figure 3). Since the formation rate of  $\text{O}_2$  was suppressed with the inclusion of  $\text{ZnGa}_2\text{O}_4$ , this indicates that suppressing  $\text{H}_2$  is the major function of  $\text{ZnGa}_2\text{O}_4$ . This result is different than that of the reported  $\text{ZnGa}_2\text{O}_4/\text{Ga}_2\text{O}_3$  heterojunction by Wang *et al.* [43].

Based on these preliminary studies, Teramura *et al.* [46<sup>•</sup>] investigated the intermediate species formed during the photocatalytic conversion of  $\text{CO}_2$  by  $\text{H}_2\text{O}$  over Ag modified  $\text{ZnGa}_2\text{O}_4/\text{Ga}_2\text{O}_3$ . They found that the partial pressure of  $\text{CO}_2$ , the concentration of  $\text{NaHCO}_3$  additives, and the reaction temperature significantly affected the photocatalytic activity and selectivity toward CO evolution. There are significant correlations between the concentration of dissolved  $\text{CO}_2$  species and the formation rates of CO. However, no obvious relationship was observed between the catalytic activities and other kinds of species, such as carbonic acid, bicarbonate, or carbonate ions. The FT-IR results indicated that bicarbonate species were formed when  $\text{CO}_2$  molecules bind to the hydroxyl groups on the surface of  $\text{ZnGa}_2\text{O}_4/\text{Ga}_2\text{O}_3$ . Among the bicarbonate species, mono-dentate bicarbonate is preferentially reduced to a bidentate formate intermediate by the electrons generated under photoirradiation. CO is then evolved from the decomposition of the generated formate.

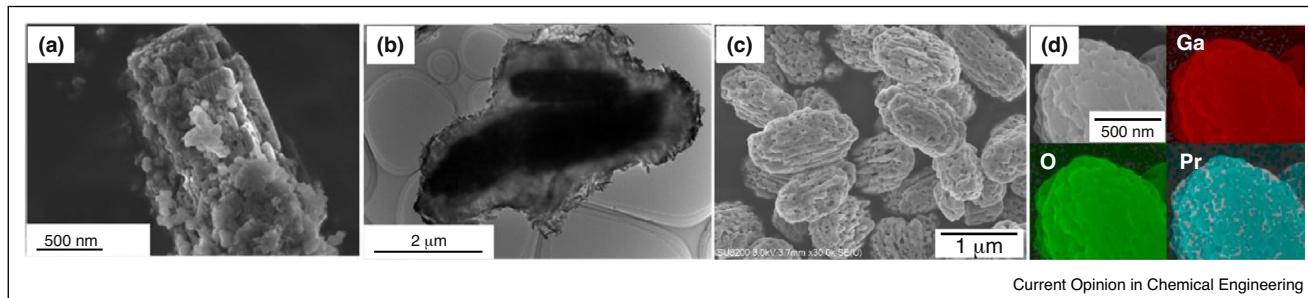
Increasing the number of active sites is another efficient way to enhance the photocatalytic activity for conversion of  $\text{CO}_2$ . As previously discussed, loading of co-catalysts has been widely used in the photocatalytic conversion of  $\text{CO}_2$ . Other strategies such as increasing the adsorption of  $\text{CO}_2$  on the surface of  $\text{Ga}_2\text{O}_3$  were shown to be useful and efficient for enhancing both the photocatalytic activity and selectivity toward CO evolution.

Iguchi *et al.* [47<sup>\*\*</sup>] designed Mg-Al layered double hydroxide (LDH) modified  $\text{Ga}_2\text{O}_3$  which showed drastically

improved the photocatalytic activity and selectivity toward CO for the conversion of  $\text{CO}_2$  in and by  $\text{H}_2\text{O}$  using a 400 W Hg lamp. LDHs are thought to be good materials for the adsorption of  $\text{CO}_2$  because of their surface basicity. Various kinds of LDHs have been reported to show photocatalytic activity for the conversion of  $\text{CO}_2$  by Iguchi *et al.* and others [48–51]. A core–shell structure was observed in the 95 mol% Mg-Al LDH modification of commercial  $\text{Ga}_2\text{O}_3$  nanorods (Figure 4a and b), which, upon loading 0.25 wt% Ag, showed the highest CO formation rate of  $211.7 \mu\text{mol h}^{-1}$ . The selectivity toward CO evolution was determined to be 61.7%. It was suggested that the modification of the Mg-Al LDH also facilitates the selective transfer of photogenerated electrons from  $\text{Ga}_2\text{O}_3$  to Ag particles to drive the conversion of  $\text{CO}_2$  to CO.

Alkali, alkaline-earth, and rare-earth metal incorporated materials can be used as bases for the adsorption of  $\text{CO}_2$  and play important roles in the surface capture of  $\text{CO}_2$ . Recently, Huang *et al.* [27<sup>\*\*</sup>] reported that praseodymium-modified gallium oxide ( $\text{Pr}/\text{Ga}_2\text{O}_3$ ) enhanced the photocatalytic activity and selectivity toward CO evolution in the conversion of  $\text{CO}_2$  in and by  $\text{H}_2\text{O}$  using a 400 W Hg lamp as compared to that of bare  $\text{Ga}_2\text{O}_3$ . It was found that  $\text{Pr}(\text{OH})_3$  and  $\text{Pr}_2\text{O}_2\text{CO}_3$  formed on the surface of  $\text{Ga}_2\text{O}_3$  after calcination of the Pr precursor at high temperature in air. These Pr species were well dispersed on the spindle-like  $\text{Ga}_2\text{O}_3$  nanoparticles after calcination (Figure 4c and d). Moreover, the Pr species facilitate  $\text{CO}_2$  capture and storage in aqueous solution of  $\text{NaHCO}_3$  with flowing  $\text{CO}_2$ . The formed Pr species with captured  $\text{CO}_2$  decomposed to CO over the  $\text{Ga}_2\text{O}_3$  photocatalyst with a Ag co-catalyst. Consequently, the Pr modified  $\text{Ga}_2\text{O}_3$  exhibited much higher activity than that of the bare  $\text{Ga}_2\text{O}_3$ . Except Pr, modification of the surface of  $\text{Ga}_2\text{O}_3$  with other rare-earth elements enhanced the evolution of CO, the selectivity toward CO also could be enhanced by further modification of the surface of the rare earth-modified  $\text{Ga}_2\text{O}_3$  with Zn [52<sup>\*</sup>].

Figure 4



SEM (a) and TEM (b) images of Mg-Al LDH modified Ga<sub>2</sub>O<sub>3</sub>. (c) Shows the Pr modified Ga<sub>2</sub>O<sub>3</sub> and the corresponding elemental mapping image (d).

Reproduced from Ref. [47\*\*] ((a) and (b)) and Ref. [27\*\*] ((c) and (d)) with permission from The Royal Society of Chemistry.

## Outlook

The development of efficient photocatalysts for the conversion of CO<sub>2</sub> is a great challenge but may help to solve the pressing issues of increasing CO<sub>2</sub> emissions and the energy crisis. The photocatalytic conversion of CO<sub>2</sub> using H<sub>2</sub>O as an electron donor is a promising method to solve the two issues simultaneously. H<sub>2</sub>O is an inexhaustible and clean electron source, which makes it an ideal choice to use for the fabrication of other highly valued chemicals such as carbon-based fuels and feedstocks. Ga<sub>2</sub>O<sub>3</sub>, as a wide bandgap photocatalyst, has sufficient reduction potential for the conversion of CO<sub>2</sub>. However, the use of Ga<sub>2</sub>O<sub>3</sub> is limited in UV range, but still shows promise for further investigation at this stage. Modification of Ga<sub>2</sub>O<sub>3</sub> with various dopants can enhance its photocatalytic activity and selectivity toward CO evolution. It is important to validate these methods and general strategies for the improvement of activity and selectivity of gallium oxide-based catalysts.

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